Progress Report

Nuclear Engineering Education Research Grant

Phase 1

"Technique Development to Support Clean-up and/or Disposal of Actinide Contaminated Soils and Sediments: Coupling Fission Track Analysis with Synchrotron X-ray Microprobe Analysis"

Sue B. Clark, Ph.D.
Washington State University
Nuclear Radiation Center and Chemistry Department
P.O. Box 644630
Pullman, WA 99164-4630

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Introduction

In this award from the U.S. Department of Energy, we have been working to develop a method to couple fission track analysis (FTA) with other *in-situ* techniques for studying actinide contamination of soils and sediments. The overall goal of this project is to develop quantitative FTA to provide images of the microscale spatial distributions of high fissile actinides (e.g., ^{235}U, ^{239}Pu) sorbed to environmental particles such as sediments and colloids. In this work, we are developing methods to provide absolute actinide surface concentrations on the particles, regardless of particle size. We are also working to provide particle size information by our approach. In future phases of our studies, we will couple our newly devised FTA methods with the quantitative determination of stable element distributions in the same particles using synchrotron x-ray microprobe analysis (SXMA).

The objectives of our work are to:

- *Develop a locator system that can be used to obtain spatial resolution of ultra-trace levels of actinides in particulate matrices representative of sediments and colloids*. This objective has been accomplished, as described below.
- For the matrices studied in Objective 1, *complete quantitative mapping of the microscale distributions of the actinides with both standards and unknown samples*. Because we know of no commercial source for standards relevant to this particular problem, these must be produced in the work proposed herein. Statistically significant numbers of sampling locations on statistically significant numbers of samples for each matrix (both standards and actual samples) must be mapped to evaluate potential sampling problems associated with quantitative analysis of heterogeneous materials (Phase 2).
- *Demonstrate that the quantitative FTA methods developed from Objectives 1 and 2 can be coupled with quantitative SXMA to determine microscale distributions of trace elements associated with the actinide depositional sites identified by the FTA approach* (Phase 3).

Progress to Date

We have devised a method for preparing soil pellets suitable for FTA. Briefly, we have demonstrated that cellulose can be used as a binder and dispersing agent into which sediments can be homogeneously mixed. This mixture can then be pressed into a pellet, into which the sediment is immobilized. The pellets are rugged enough for normal handling and can be archived for later use. Also, in our reactor we have irradiated the cellulose used in our process; it does not activate to any significant degree and does not create interferences that would be problematic for FTA or SXMA. We have pellets we prepared over 9 months ago that show no signs of degradation, even after the brief periods of irradiation necessary for FTA.

For FTA, we need the sediment or colloids to be immobilized on the surface of the pellet. To obtain the image shown in **Fig. 1**, we prepared a pellet composed of only cellulose in a hydraulic press using a 10 cm die. After pressing the pellet, the die was opened and the pellet left in place. Onto the surface of the pellet, soil particles from Rocky Flats were added, the die was resealed, and the pellet was pressed a second time. This sample was placed in contact with a Lexan track detector and irradiated. The Lexan detector was then developed with chemical etching, and observed under a microscope. The fission track image is shown in Figure 1.

To develop a locator system for FTA, we are using technology employed in scanning electron microscopy (SEM). In SEM, locator grids are often used to record absolute locations of very small features, which can then be located again later. These grids, made of copper, are not visible by FTA. However, we have solved this problem using the $^{10}B(N\alpha)^{10}Li$ nuclear reaction similar to the approach of Morris et al. [1988]. We can now electrodeposited boron onto an copper SEM locator grid. The grid is clamped to stainless steel tweezers, attached to the anode of a potentiometer, and submerged into a 4% (saturated) boric acid solution. A platinum wire serves as the cathode. Boron was deposited onto the copper with 2.4 volts for 1 hour. The formation of a blue color on the grid indicated that boronation was complete. These boronated grids can be pressed onto the surface of the sediment-containing pellet. With optimal irradiation

and etching time, an image of the locator grid is created in the Lexan from α tracks, as shown in **Figure 2**.

Another method for obtaining an image of the grid in the track detector is to coat the SEM grid with ^{235}U. This gives excellent images of the grid, but presents some concerns for cross contamination for samples that contain ^{235}U. This limitation needs to be explored more fully before ^{235}U is used routinely on the grids.

We have used the grid images to obtain locations of ^{235}U- and ^{239}Pu-ladened particles (also called "hot" particles_, as shown in **Figure 3**. This demonstrates that the fission tracks from the grids can be correlated with fission tracks resulting from the high fissile actinides. The locator grid remains attached to the pellet itself, providing an easy method for locating the exact particle in the sample that was responsible for creating the fission tracks in the Lexan.

For the sample with which the image in Figure 3 was obtained, we collected an SEM image in that same location, as shown in **Figure 4**. The bright spot in the SEM image is the same spot observed as the "hot" particle revealed by FTA. Further magnification of this location in the sample shows a material that is different from the surrounding material. The composition of this material is unknown, but this will be explored in Phase 2 of our work.

Work Plan – Phase 2

In Phase 2, we propose to address the quantitative issues associated with surface concentration and particle size. Using the methods developed from Phase 1, we will complete FTA on additional particles, and develop quantitative correlations between the numbers of tracks scored by the automated system, the density of tracks associated with a specific size of particles, and the size of the particles used. From this information, we will determine a surface concentration of ^{235}U or ^{239}Pu, and we will be able to correlate track density with particle size. Although conceptually this task appears relatively straightforward, obtaining information that is quantitative will require a significant level of effort. We will use an approach similar to Priest et al. [1992], which will involved the analysis of multiple samples of each particle size for each isotope

studied. With each sample, multiple sites on the track detector must be analyzed. For example, Priest et al. scored at least 200 sites for every sample analyzed. We intend to target particle size ranges on the order of less than 0.08 μm, 0.08 – 0.2 μm, 0.2 – 2 μm, and 2 – 5 μm. We will also use this quantitative approach developed in Phaser 2 to study Pu distributions in some of the actual sediments we have studied using sequential extractions.

This work is of interest to various DOE sites, and we have begun a collaboration with scientists at INEEL to apply our work to their soils and sediments. The collaboration is funded by the Inland Northwest Research Alliance (INRA), and allows us to develop applications of the fundamental research funded by NEER. In the joint NEER/INRA work, we will expand our Phase 2 activities described above to include analysis of INEEL soils and sediments taken from locations such as Pit 9 and other locations in the Radioactive Waste Management Complex (RWMC). Information from our FTA work will be useful to INEEL scientists for developing soil remediation strategies at INEEL.

Project Deliverables To Date

Students Trained: This project is closely related to another projected in my laboratory that is funded by the Inland Northwest Research Alliance. Through these two projects, two graduate students and a post-doctoral fellow have been trained in radiochemistry and nuclear science. One of the students, Dr. Stacey Loyland, has finished her Ph.D., and is now employed by DOE's Environmental Measurements Laboratory. The post-doctoral student, Dr. Steve Lamont, has accepted a position at DOE's Savannah River Site, working for Westinghouse Savannah River Technology Center.

Papers Published: The following manuscript has been accepted for publication:

S. M. Loyland Asbury, S. P. Lamont, and S. B. Clark (in press), "Plutonium Partioning to Colloidal and Particulate Matter in an Acidic, Sandy Sediment: Implications for Remediation Alternatives and Plutonium Migration", Environmental Science and Technology

Presentations: The following presentation will be made at the American Nuclear Society Meeting to be held June 18-22, 2001:

> "New Methods to Support Clean-up of Plutonium Contaminated Soils and Sediments," S. B. Clark, H. Kurosaki, S. Lamont, S. M. Loyland Asbury, and R. Filby, Washington State University, Department of Chemistry and Nuclear Radiation Center, P.O. Box 644630, Pullman, WA 99164-4630

Project Delays and Difficulties

The only delay experienced to date is with the purchase of the FTA equipment, which was requested and funded in Phase 1. This equipment purchase involves the upgrade of existing equipment, which belonged to Dr. Ed Kaplan of Brookhaven National Laboratory. Although we worked constantly and diligently with Dr. Kaplan to have the equipment transferred from BNL to WSU, this only occurred within the last month. The equipment has now been released to us, and has been sent to the company to be upgraded. The money for the upgrade has been encumbered, but final payment has not yet occurred.

Literature Cited

Morris, K. J. and A. L. Batchelor, 1988. "The Simultaneous imaging of boronated tissue sections and the location of fissionable actinides particles in CR 39 solid state track detectors.", *Phys. Med. Biol.,* **33** 1195-1203.

Priest, N. D., J. W. Haines, J. A. M. Humphries, H. Metivier, and R. L. Kathren, 1992. "The bone volume effect on the dosimetry of ^{239}Pu and ^{241}Am in the skeleton of man and baboon." Journal of Radioanalytical and Nuclear Chemistry, **156**, 33-53.

Wong, R., W. C. Burnett, S. B. Clark, and B. S. Crandall , 1999. "An improved assay for the determination of gross alpha and beta activities in soil via liquid scintillation counting, " *in:* Environmental Radiochemical Analysis (Ed., G. W. A. Newton) Royal Society of Chemistry, Special Publication No 234, 242-264.

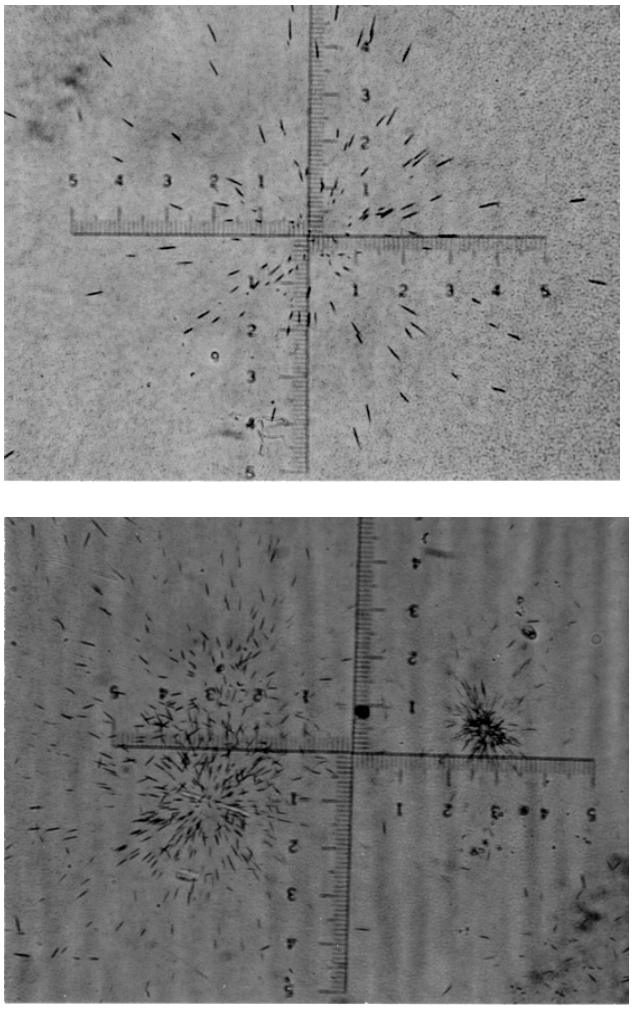

Figure 1: Fission track analysis of a sediment from Pond B at the Savannah River Site. The sediment was immobilized into a cellulose pellet as described by Wong et al., 1999. The pellet was then irradiated in contact with a Lexan track detector for approx. 7 minutes with a neutron fluence of 10^{13} neutrons · cm^{-3} at WSU's 1 MW TRIGA-fueled research reactor.

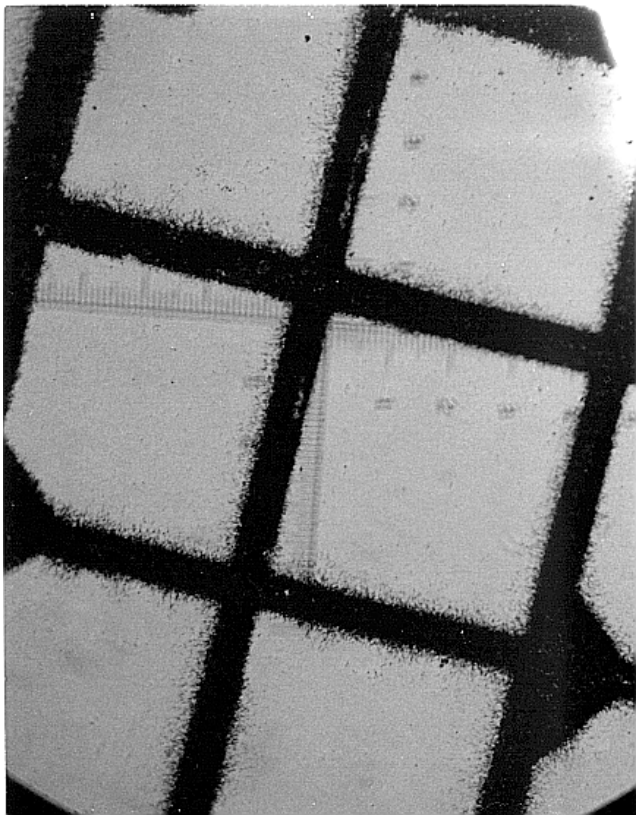

Figure 2: Fission track image of a boronated SEM grid (see text for details about preparation). The grid is the basis for the locator system we have developed. The triangle shapes in the grid are used to map absolute locations, allowing identification of exact locations on a submicron scale.

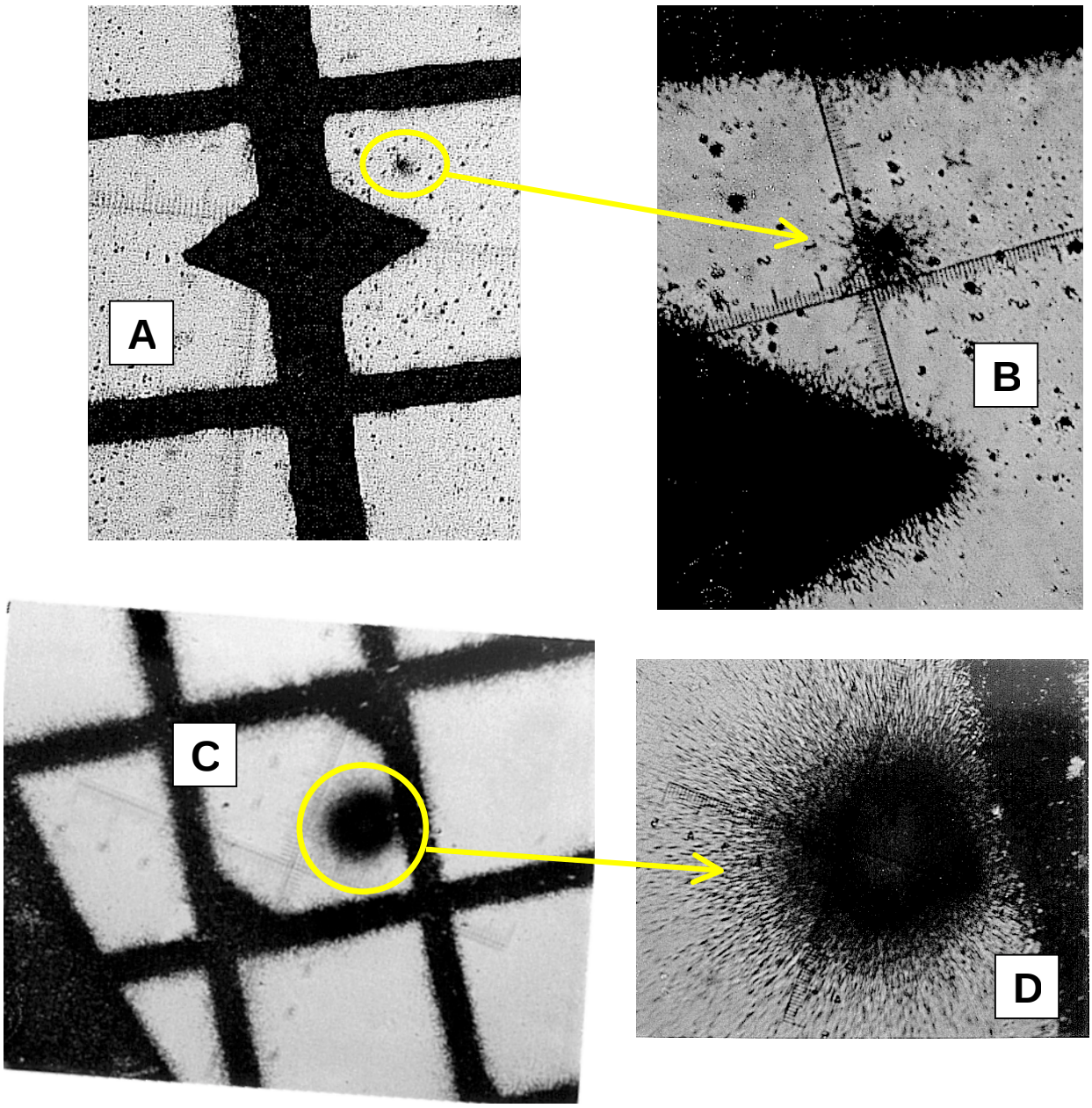

Figure 3: Fission track images of SEM grids and ^{235}U- and ^{239}Pu-ladened particles. A. FTA of an SRS sediment. The SEM grid is clearly evident, along with a very small "hot" particle containing either ^{235}U or ^{239}Pu. B. The tracks from hot particle in A enlarged. C. FTA of a sediment from Rocky Flats, showing a "hot" particle. D. An enlargement of the tracks from the particle shown in C.

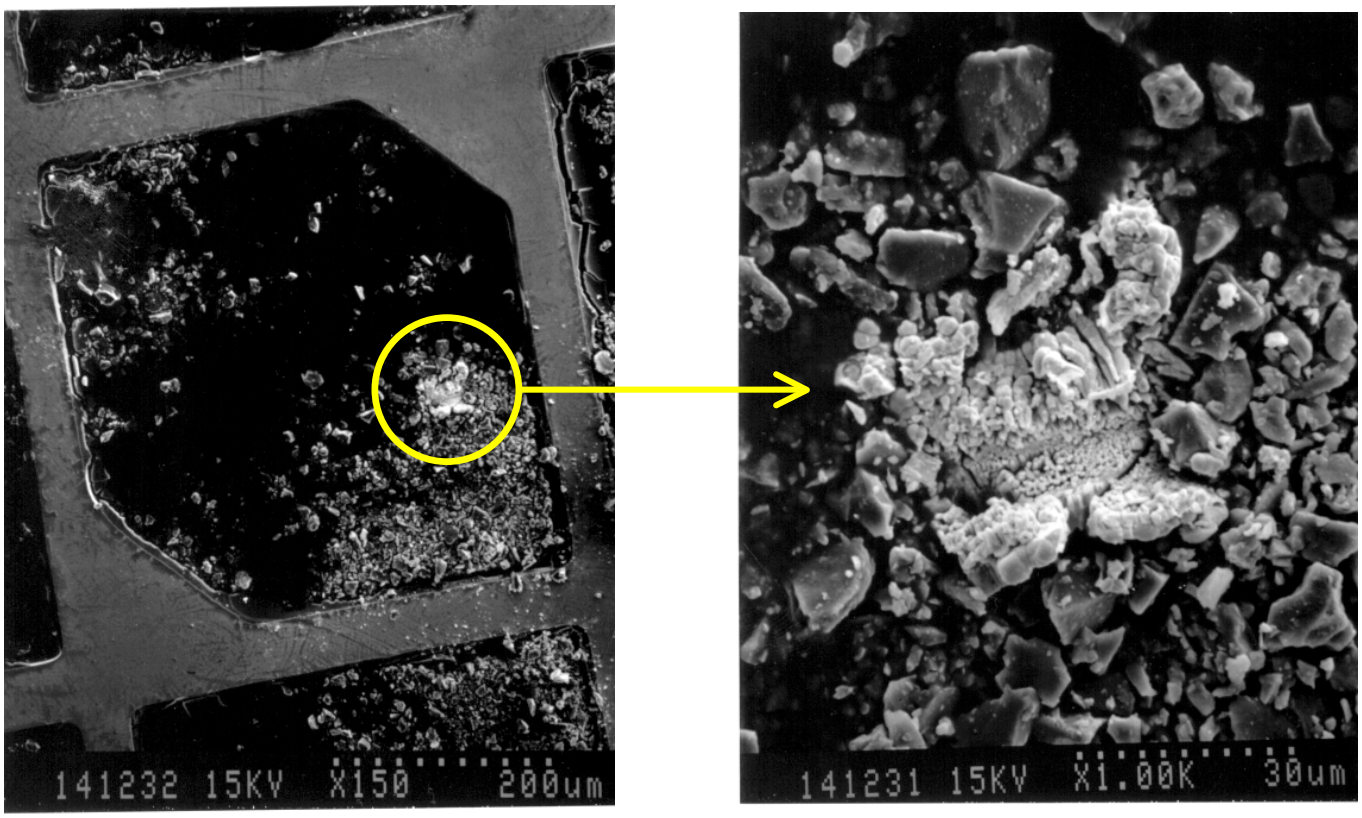

Figure 4: An SEM image of the particle that created the tracks shown in Figures 3C and 3D. Notice that the SEM image shown above and the FTA image shown in Figure 3C are almost exact overlays. It is also clear from the SEM images that the "hot" particle material is different from the other, surrounding material. Obtaining chemical analysis of the "hot" particle material *in-situ* using SXMA is the focus of the work for Phases 2 and 3 in this research program.